UNPUBLISHED PRELIMINARY DATA

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For the period October 1, 1964 to March 31, 1965; NASA Research Grant NsG-512 to the University of Florida for basic scientific research on the subject:

"Quantum Theory Studies of the Energies of Excited State Atoms and Molecules, Particularly as They Occur in the Upper and Stellar Atmospheres, and in Materials Undergoing Combustion".

Perhaps the most significant development during the past six months is the refinement of criteria and methods for calculating lower bounds to eigenvalues. The current status of this and other projects and our plans for the next six months are summarized.

Upper and Lower Bounds to Energy Eigenvalues: Preprints for two papers are enclosed:

> "Studies in Perturbation Theory IX. Connection Between Various Approaches in the Recent Development", by P. O. Löwdin. Preprint No. 53. June 1, 1964.
>
> "Studies in Perturbation Theory X. Lower Bounds to Energy Eigenvalues in Perturbation Theory", by P. O. Löwdin. Preprint No. 64. June 1, 1964.

These papers give a short survey of the history of the problem of evaluating lower bounds to the energy eigenvalues E to the Schrödinger equation $\mathcal{H}\Psi = E\Psi$, and the new results obtained by us so far. In Perturbation Theory X, we studied the problem of evaluating the ground state energy of $\mathcal{H} = \mathcal{H}_0 + V$ in case the conditions

$$V > 0 \quad , \quad \mathcal{E} < E_1^0$$

were fulfilled. Here $\mathcal{E}$ is an upper bound to the ground state energy and should be less than the energy of the first excited state E_1^0. We have now extended the theory to excited states, and the restriction

$\epsilon < E_1^o$ is relaxed. Applications to physical problems of these lower bound methods are reported in the following manuscripts, which are under preparation:

> "Lower Bounds to the Eigenvalues for the Stark Effect in a Rigid Rotator", by J. H. Choi and D. W. Smith.
>
> "Lower Bounds for the Energy Values of Anharmonic Oscillators", by C. E. Reid.
>
> "Upper and Lower Bounds for the Eigenvalues of a Double Minimum Potential", by C. Bunge and A. Bunge.

Further applications which are underway are the Z^{-1} expansions of two-electron ions, (Goscinski), the H^- problem (Choi), and the excited triplet states of He (Wilson).

Intramolecular Relaxation Processes: A manuscript entitled

> "The Theory of Intramolecular Relaxation Processes" by Ludwig Hofacker

is enclosed. Part of this work was carried out at the University of Florida during the Fall of 1963.

Calculations on CH^+ and O_2: The work discussed in the last report is being continued, and will be reported in more detail in the next status report.

Series Expansion of Eigenvalues: (Reid and Saavedra) In $\frac{1}{Z}$ expansions of electronic wave functions for He-like ions, preliminary

results have been obtained for both ground and excited singlet states. Only radial basis functions have been used so far, but the extension to include angular functions is underway, as is the extension to triplet states.

Natural Orbitals for Two-Electron Systems: (Reid and Wilson) A scaling procedure based on a method of Löwdin's (J. Mol. Spect. 13, 326, 1964) has proved successful for calculating natural orbitals for two-electron systems. The convergence is so rapid that only two or three iterations at most have been needed. Natural orbitals for the radial-limit wave functions for two-electron atoms and ions up to C^{+4} have been calculated for the ground state and several excited states.

Molecular Calculations--Large Systems: (Conklin) By dividing space into several regions and expressing the total wave-function in each such region in terms of convenient basis functions about one center for that region, the many-center problem so common in molecular calculations is exchanged for a boundary-value problem. It seems quite possible that this boundary-value problem (matching the amplitude and first derivative of the wave-function along the boundaries of the various regions) may be considerably more tractable than the many-center problem. Dr. Conklin is currently investigating Slater's APW method for calculating one-electron wave-functions for crystalline solids, and studying some of the programming techniques useful for carrying out APW calculations. Although the specific expansions used in the APW scheme will require some modification for application to the molecular problem, it seems quite possible that many of the approaches and some of the specific programs used in applying the APW scheme to actual calculations may be useful in the molecular problem if this idea is to be used for calculations.

He is developing computer programs for generating functions (for instance, the spherical Bessel functions which may well appear in the molecular case also), and group theory techniques, which may be

worth carrying over for molecules of sufficiently high symmetry.

The Alternant Molecular Orbital Method: (Pauncz) In applying the method of different orbitals for different spins (DODS) to diatomic molecules, it seemed worthwhile to first consider some problems inherent in the method. A comparison with the non-paired spatial orbital (NPSO) method has been made and it was found that the NPSO method gives better results for small conjugated systems, but the AMO method has wider possibilities for application. A manuscript entitled:

"Recent Developments in the Method of Different Orbitals for Different Spins" by Ruben Pauncz

is enclosed.

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